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Syntheses and Structures of Terminal Arylalumylene Complexes

*Koichi Nagata, Tomohiro Agou, and Norihiro Tokitoh**

Dedicated to Prof. Renji Okazaki on the occasion of his 77th birthday.

Abstract: *Terminal arylalumylene complexes of platinum [Ar–Al–Pt(PCy$_3$)$_2$] (Ar=Bbp or Tbb, Bbp=2,6-[CH(SiMe$_3$)$_2$]$_2$C$_6$H$_3$, Tbb=2,6-[CH(SiMe$_3$)$_2$]$_2$-4-(t-Bu)C$_6$H$_2$) have been synthesized by the reaction of a dialumene–benzene adduct with [Pt(PCy$_3$)$_2$] or by the reduction of 1,2-dibromodialumanes Ar(Br)Al–Al(Br)Ar in the presence of [Pt(PCy$_3$)$_2$]. X-Ray crystallographic analysis revealed that the Al–Pt bond lengths of these arylalumylene complexes are shorter than the previously reported shortest Al–Pt distance. DFT calculations suggested that the Al–Pt bonds in the arylalumylene complexes have significantly high electrostatic character rather than covalent character.*

Transition metal complexes of subvalent main group element compounds attract considerable attention, because of not only their unique electronic structures but also their synthetic potentials in organometallic chemistry. Especially, complexes of group 13 metallylenes (:ER, E = B, Al, Ga, In, and Tl) are expected to show particular bonding interactions between the subvalent group 13 elements and transition metal fragments, since these metallylenes posses a lone pair and two vacant p orbitals and may act as σ-donor/π-acceptor ligands.[1] Recently, the chemistry of borylene complexes has been extensively developed,[2] while the examples of heavier group 13 metallylene complexes with the formula of [M(ER)$_m$L$_n$] (R: anionic monodentate ligands) have been limited for the gallium and indium homologues and are yet to be reported for aluminum.[3] Although Lewis base-coordinated terminal alumylene complexes (*e.g.*, complexes **I**, **II**, and **III** in Figure 1) have been synthesized as stable compounds,[4-7] there has been no alumylene complexes featuring two-coordinated subvalent aluminum moieties (*i.e*, complex **IV**). Because the coordination of Lewis bases may mask the intrinsic nature of the alumylene ligands, it has been desired to develop Lewis base-free alumylene complexes in order to elucidate the bonding situation between the alumylene and transition metal moieties. Herein, we report the syntheses and structures of platinum complexes of arylalumylenes, which are the first examples of Lewis base-free alumylene complexes.

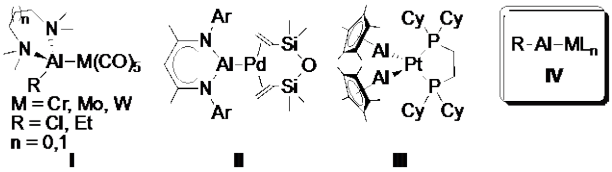
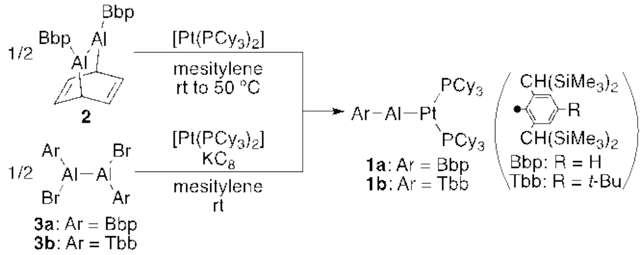


Figure 1. Transition metal complexes of Lewis base-coordinated (**I**-**III**) and Lewis base-free (**IV**) alumylenes. Ar = 2,6-(*i*-Pr)$_2$C$_6$H$_3$.

Recently, we have communicated a reactivity of dialumene–benzene adduct **2** as a synthetic equivalent of diaryldialumene BbpAl=AlBbp.[8,9] During the research on the reactivities of **2**, the reaction of **2** and [Pt(PCy$_3$)$_2$] was investigated with the expectation of trapping of the dialumene as a π-dialumene complex of platinum.[10] The reaction progress was monitored by ^{31}P NMR spectroscopy, showing the formation of a mixture containing a new platinum complex (δ□=69.9 ppm). Fractional crystallization of the crude material from *n*-hexane at –35 ºC yielded a small amount (3%) of arylalumylene complex **1a** as air- and moisture-sensitive dark red crystals (Scheme 1). The formation of **1a** implies that compound **2** has reactivities as an arylalumylene source in addition to the diaryldialumene synthon. After screening of the reaction conditions, finally, reduction of 1,2-dibromodialumanes **3a**[11] and **3b** with KC$_8$ in the presence of [Pt(PCy$_3$)$_2$] was found to afford **1a** and **1b**, respectively, as sole products. After recrystallization from *n*-hexane at –35 ºC, the arylalumylene complexes were obtained in moderate yields (**1a**: 72%, **1b**: 21%). Complexes **1a** and **1b** are stable up to 79 and 110 ºC in the solid state, respectively, though they slowly decompose in solution even at –35 ºC to give complicated mixtures containing [Pt(PCy$_3$)$_2$] and PCy$_3$.



Scheme 1. Syntheses of arylalumylene complexes **1a** and **1b**.

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

In the ^{31}P NMR spectra, complexes **1a** and **1b** exhibit singlet signals accompanied by ^{195}Pt satellites at δ=69.9 ppm ($^1J_{PPt}$=4015 Hz) and at δ=69.8 ppm ($^1J_{PPt}$=4033 Hz), respectively, which are downfield shifted with respect to those of [Pt(PCy$_3$)$_2$] (δ=62.3 ppm, $^1J_{PPt}$=4160 Hz) and the structurally related carbonyl complex [(Cy$_3$P)$_2$Pt(CO)] (δ=63.7 ppm, $^1J_{PPt}$=4101 Hz).[12] Definite signals could not be observed in the ^{27}Al and ^{195}Pt NMR spectra of complexes **1a** and **1b**, probably because of the signal broadening caused by the high quadrupole moment of the ^{27}Al nuclei.

Molecular structures of complexes **1a** and **1b** were determined by X-ray crystallographic analyses, showing that the aluminum atoms are definitely two-coordinated and are bound to the platinum atoms in terminal fashions with the C1–Al1–Pt1 angles of 179.2(2) (**1a**) and 173.96(14)º (**1b**) (Figure 2). The platinum centers adopt distorted trigonal planar geometries. The Pt1–Al1 bonds of the arylalumylene complexes (**1a**: 2.2857(18) Å, **1b**: 2.2829(13) Å) are slightly shortened compared with the shortest Pt–Al distance previously reported (2.327(2) Å),[6e] most likely due to the decreased coordination number of platinum as well as the difference in the aluminum-bound substituents.[13]

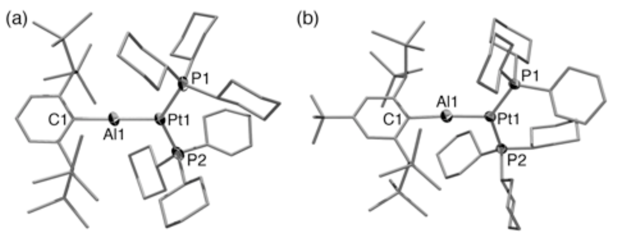

Figure 2. Molecular structures of (a) **1a** and (b) **1b**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted, and Bbp, Tbb, and Cy group are shown in wireframe format for clarity. Three Cy and two Me groups in complex **1a** were disordered over two positions (see the Supporting Information for detail). Selected bond lengths [Å] and angles [º]: (for **1a**) Al1–Pt1 2.2857(18), C1–Al1 2.001(6), Pt1–P1 2.2828(17), Pt1–P2 2.2903(16), C1–Al1–Pt1 179.2(2), Al1–Pt1–P1 114.86(6), Al1–Pt1–P2 117.85(6), P1–Pt1–P2 127.29(6); (for **1b**) Al1–Pt1 2.2829(13), C1–Al1 1.986(4), Pt1–P1 2.3071(9), Pt1–P2 2.2673(10), C1–Al1–Pt1 173.96(14), Al1–Pt1–P1 119.14(4), Al1–Pt1–P2 109.20(4), P1–Pt1–P2 131.56(4).

To gain further information on the bonding situation in **1a** and **1b**, density functional theory (DFT) calculations at the M062X[14]/SDD[Pt]:6-311G(2df)[Al,P]:6-31G(d)[Si,C,H] level were performed on a real molecule of **1a**. The comparison of the optimized and experimental bond lengths and angles of **1a** shows that the DFT-optimized structure well reproduces that found in the single crystals. The natural bond orbital (NBO) analysis[15] on the optimized geometry of **1a** showed that the Al–Pt bond has a small Wiberg bond index (0.59), indicating that the Al–Pt bond is highly ionic and that the contribution of the covalent interaction is less important.[6e,16] The calculated NBO corresponding to the Al–Pt bond is predominantly formed from the overlap of the 3s(Al) and 6s(Pt) orbitals (σ(Al–Pt)=0.87(3s3p$^{0.03}$)Al+0.50(6s6p$^{0.03}$6d$^{0.02}$)Pt). Meanwhile, the Pt→Al π-back donation interactions were identified as donor/acceptor interactions, and the stabilization energies by the two 5d(Pt)→3p(Al) π-back donations were estimated to be 19.86 and 4.54 kcal mol^{-1} by the second-order perturbation theory analysis. The nature of the Al–Pt bond in **1a** was further investigated in terms of the energy decomposition analysis,[17,18] showing that the Al–Pt bonding interaction is mainly electrostatic. The electrostatic interaction contributes 74.0% of the total attractive interactions between the BbpAl and [Pt(PCy$_3$)$_2$] moieties. The breakdown of the Al–Pt orbital interaction energy into σ- and π-components indicates that the Al π→Pt back donation significantly contributes to the covalent bonding (σ: 55.8%, π: 44.2%).

In summary, the first Lewis base-free terminal arylalumylene complexes were obtained by two different routes: the treatment of the dialumene–benzene adduct with [Pt(PCy$_3$)$_2$] and the reduction of the 1,2-dibromodialumanes in the presence of [Pt(PCy$_3$)$_2$]. The Al–Pt bonds in the arylalumylene complexes were shortened compared to the previously reported Al–Pt distances, indicating the stronger bonding interactions between the alumylene and platinum moieties. The DFT calculations suggested that the Al–Pt bonds in the arylalumylene complexes possess significantly high electrostatic character and that the contribution of the Pt→Al π-back donation to the covalent interactions is comparable to that of the Al σ→Pt donation.

Experimental Section

All the manipulations were performed under a dry argon atmosphere by using the Schlenk techniques and glove boxes. Solvents were purified by the Ultimate Solvent System, Glass Contour Company[19] (*n*-hexane) or by the bulb-to-bulb distillation from a potassium mirror (C_6D_6 and mesitylene). [Pt(PCy$_3$)$_2$] was prepared according to a literature.[20]

Reaction of **2** with [Pt(PCy$_3$)$_2$]: A solution of **2** (13.4 mg, 0.0124 mmol) and [Pt(PCy$_3$)$_2$] (17.4 mg, 0.0230 mmol) in mesitylene (2 mL) was stirred at room temperature for 2.5 h and then at 50 ºC for 2 h, affording a mixture containing **1a** and [Pt(PCy$_3$)$_2$] in a ratio of *ca*. 1.0:1.5. Small amount of pure **1a** (1.0 mg, 0.00085 mmol, 3%) was obtained by fractional crystallization from *n*-hexane at –35 ºC.

Reduction of **3a** in the presence of [Pt(PCy$_3$)$_2$]: To a mesitylene (5 mL) solution of **3a** (13.2 mg, 0.013 mmol) and [Pt(PCy$_3$)$_2$] (19.0 mg, 0.025 mmol) was added KC$_8$ (3.8 mg, 0.028 mmol). The mixture was stirred at room temperature for 4.5 h. After removal of the solvents, the residue was extracted with *n*-hexane and filtered. The filtrate was concentrated and stored at –35 ºC to give **1a** as dark red crystals (22.2 mg, 0.019 mmol, 72%). m.p. 79 ºC (dec.); ^{1}H NMR (600 MHz, C_6D_6): δ=0.29 (s, 36H, Si(C*H*$_3$)$_3$), 1.22-1.43 (m, 24H, *Cy*), 1.65-1.73 (m, 18H, *Cy*), 1.90-1.92 (m, 12H, *Cy*), 2.20-2.22 (m, 12H, *Cy*), 2.75 (s, 2H, C*H*(SiMe$_3$)$_2$), 6.78 (d, ^3J = 7.7 Hz, 2H, *m*-Ar*H*), 7.08 (t, ^3J = 7.7 Hz, 1H, *p*-Ar*H*); ^{13}C{^{1}H} NMR (151 MHz, C_6D_6): δ=1.28 (s, Si*Me*$_3$), 27.1 (s, C^4(Cy)), 28.3 (virtual triplet, J_{CP} = 4.5 Hz, $C^{2,6}$(Cy),), 31.2 (s, *C*H(SiMe$_3$)$_2$), 31.3 (s, $^4J_{CPt}$ = 24.1 Hz, $C^{3,5}$(Cy)), 41.3 (virtual triplet, J_{CP} = 9.1 Hz, $^2J_{CPt}$ = 36.2 Hz, C^1(Cy)), 123.9 (s, $^4J_{CPt}$ = 22.7 Hz, *m*-*C*(Ar)), 129.22 (s, *p*-*C*(Ar)), 149.4 (s, *o*-*C*(Ar)), 160.0 (t, $^3J_{CP}$ = 25.7 Hz, *ipso*-*C*(Ar)); ^{31}P NMR (120 MHz, C_6D_6): δ=69.9 (s, $^1J_{PPt}$ = 4015 Hz); UV/vis (hexane): λ=447 (ε 1600), 488 (ε 1800) nm; UV/vis (THF): λ=446 (ε 1400), 489 (ε 1500) nm; HRMS (DART-TOF, positive mode) *m*/*z* calcd. for [$C_{56}H_{107}AlP_2Si_4{}^{195}Pt$]$^+$: 1175.6388; found: 1175.6412.

1b: As described for the reduction of **3a**, a mesitylene (5 mL) solution of **3b** (21.5 mg, 0.0193 mmol) and [Pt(PCy$_3$)$_2$] (29.1 mg, 0.0386 mmol) was treated with KC$_8$ (5.3 mg, 0.039 mmol). After workup and recrystallization, **1b** was obtained as dark red crystals (10.0 mg. 0.0082 mmol, 21%). m.p. 110 ºC (dec.); ^{1}H NMR (600 MHz, C_6D_6): δ=0.32 (s, 36H, Si(C*H*$_3$)$_3$), 1.20-1.44 (m, 24H, *Cy*), 1.35 (s, 9H, C(C*H*$_3$)$_3$), 1.68-1.72 (m, 18H, *Cy*), 1.90-1.92 (m, 12H, *Cy*), 2.21-2.23 (m, 12H, *Cy*), 2.72 (s, 2H, C*H*(SiMe$_3$)$_2$), 6.81 (s, 2H, *m*-Ar*H*); ^{13}C{^{1}H} NMR (151 MHz, C_6D_6): δ=1.30 (s, Si*Me*$_3$), 27.1 (s, C^4(Cy)), 28.3 (virtual triplet, J_{CP} = 4.6 Hz, $C^{2,6}$(Cy)), 31.0 (s, *C*H(SiMe$_3$)$_2$), 31.2 (s, $C^{3,5}$(Cy)), 31.4 (s, C*Me*$_3$), 34.5 (s, *C*Me$_3$), 41.4 (virtual triplet, J_{CP} = 8.3 Hz, C^1(Cy)), 121.3 (s, $^4J_{CPt}$ = 22.7 Hz, *m*-*C*(Ar)), 149.0 (s, *p*-*C*(Ar)), 151.1 (s, *o*-*C*(Ar)), 157.0 (t, $^3J_{CP}$ = 27.2 Hz, *ipso*-*C*(Ar)); ^{31}P NMR (243 MHz, C_6D_6): δ=69.8 (s, $^1J_{PPt}$ = 4033 Hz); UV/vis (hexane): λ =447 (ε 1700), 483 (ε 1900) nm; UV/vis (THF): λ=447 (ε 1500), 483 (ε 1600) nm; HRMS (DART-TOF, positive mode) *m*/*z* calcd. for [$C_{60}H_{115}AlP_2Si_4{}^{195}Pt$]$^+$: 1231.7021; found: 1231.7026.

Single crystals of **1a** and **1b**•hexane were obtained by cooling their saturated solutions in *n*-hexane to –35 ºC. The crystal data of **1a** was collected on a Rigaku Saturn 70 CCD diffractometer with a VariMax Mo Optic System using a Mo *K*α radiation (λ=0.71070 Å), while that of

1b•hexane was collected at the BL38B1 beamline of the SPring-8 using an ADSC Quantum 315 CCD detector and Si(111)-monochromated X-ray radiation (λ=0.85000 Å). The structures were solved with the Shelx program package.[21] Crystal data for **1a**: monoclinic , space group $P2_1/c$, –173 ºC, a=13.1525(3), b=19.5941(4), c=24.5674(5) Å, β=96.2678(15), V=6293.5(2) Å^3, Z=4, μ=2.402 mm^{-1} (λ=0.71070 Å), 2.08º<θ<25.50º, R_{int}=0.0845, Completeness to θ_{max} 99.9%, 760 parameters refined, R_1 (I>2σ(I))=0.0456, wR_2 (all data)=0.1110, GOF=1.018, largest diff. peak and hole 1.917 and –1.714 e Å^{-3}. Crystal data for **1b**•hexane: triclinic, space group P-1, –170 ºC, a=12.5246(1), b=13.9973(2), c=21.9295(3) Å, α=89.9651(6), β=83.0595(5), γ=73.3812(6)º, V=3654.56(8) Å^3, Z=2, μ=0.243 mm^{-1} (λ=0.85000 Å), 2.05º<θ<31.00º, R_{int}=0.0507, Completeness to θ_{max} 99.0%, 683 parameters refined, R_1 (I>2σ(I))=0.0423, wR_2 (all data)=0.1172, GOF=1.086, largest diff. peak and hole 1.253 and –2.204 e Å^{-3}. CCDC-948098 (**1a**) and 948113 (**1b**•hexane) contain the supplementary crystallographic data for this paper. These date can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Entry for the Table of Contents

Aluminum Complexes

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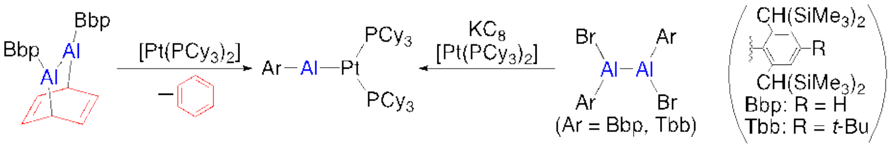
Syntheses and Structures of Terminal Arylalumylene Complexes



A terminal arylalumylene complex of platinum was obtained by the reaction of a dialumene–benzene adduct and $[Pt(PCy_3)_2]$. Reduction of 1,2-dibromodialumanes in the presence of $[Pt(PCy_3)_2]$ also afforded the terminal arylalumylene complexes. DFT calculations suggested that the Al–Pt bonds in the arylalumylene complexes have significantly high electrostatic character rather than covalent character.